The Time Interval between Absorption and Emission of Light in Fluorescence.

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(Received June 12, 1921.)

[Plate 5.]

The more recent theories of the absorption and emission of light, as in cases of resonance radiation and fluorescence, make the two processes quite distinct. According to Bohr the absorption of radiation of frequency corresponding to D_2 by non-luminous sodium vapour, is associated with the passage of an electron from an inner to an outer stable orbit; resonance radiation resulting when the electron returns to the original orbit. The time interval between these two processes is probably too short to be detected experimentally, for the faintness of the light makes it appear doubtful whether methods, similar to the one devised by Abraham and Lemoine, can be used in these cases. In the case of the fluorescence, or rather phosphorescence, of mercury vapour, I have succeeded in measuring the time interval, the vapour remaining non-luminous during the process of the absorption of light, and bursting into luminosity about 1/15000th of a second later. This, I believe, is the first case ever observed of a photo-luminescent body remaining dark during the period of excitation.

In the study of processes of this nature two methods are available: we may give the substance a very high velocity of translation or rotation and cause it to pass through a very narrow and intense beam of light, or we may keep the substance stationary, illuminating it with flashes of very brief duration and examining it during the moment of excitation, or at definite moments later, through a perforated disc rotating at high speed (phosphoroscope). Both methods have been employed in the present work, the former being preferable in some respects.

The fluorescence of mercury vapour is bluish green in colour and results from the absorption of ultra-violet light in the region of very short wavelengths (1850–2100). It would seem probable, in view of Steubing's results on the ionization of the fluorescing vapour, that the absorption of light causes the expulsion of an electron, the fluorescence resulting from its return to the atom. The phenomenon, however, is probably not as simple as this, for monatomic mercury vapour in equilibrium with the metal, or when no fluid metal is present, does not exhibit fluorescence at any density or temperature.

The fluorescence appears only in the case of vapour *freshly liberated from the fluid metal,* probably diatomic mercury. This is indicated by the circumstance that when an exhausted quartz bulb containing a drop of mercury is very gradually heated in an electric oven, fluorescence is barely visible at 170° and rises to great intensity at 180° (certainly a ten-fold increase in intensity). The vapour density, with this rise of temperature, increases from 8 mm. to 11 mm. If, now, the oven is allowed to cool, fluorescence disappears as soon as the temperature has fallen two degrees, *i.e.*, as soon as condensation begins.

The fact has been still more clearly shown in some recent work done in collaboration with Mr. J. S. van der Lingen, in which the mercury is contained in a double bulb connected by a short tube. One bulb is at 200°, the other at 205°, the mercury gathering in the cooler bulb. Both are illuminated by a spark and no fluorescence is observed. If the hot bulb is now suddenly cooled by an air blast, the other bulb immediately shows brilliant fluorescence, for the mercury in it immediately begins to vapourize. The absorption, however, appears to be a characteristic of the atom, at least I have never been able to detect any difference between the absorption of freshly forming vapour, and that of vapour in a static condition.

The time interval which elapses between the absorption and emission of the light can be easily observed in the following way: a tube of fused quartz of the form shown in Plate 5, fig. 1 (with a total length of 15 cm. and a bore of 4 mm.) containing about 1 c.c. of mercury, is exhausted and sealed. The tube should be heated during the exhaustion and the metal boiled. It is mounted in a clamp-stand and the mercury bulb heated by a Bunsen flame about 1 cm. in height. An aluminium spark (condensed discharge) is arranged as shown in the figure, the light passing through a hole 2 mm. in diameter in a thin metal plate mounted close to the tube. The cylindrical beam of light should pass through the centre of the tube, which can be accomplished by observing the circular illuminated patches where it passes through the walls. On lighting the burner, as soon as active distillation of the mercury commences, we observe a faint greenish light filling the entire tube. This is the phenomenon observed by Phillips[*] with a tube of similar form, excited, however, by the 2536 line of the mercury arc.

As the temperature of the " condenser " end of the tube rises, the velocity of the vapour becomes less, the luminosity draws down towards the illuminated region, and presently appears in the form of a beautiful green flame, concave on the under side as shown in Plate 5, fig. 1. The flame form is due obviously to the high velocity of the vapour along the axis of the tube, and the low velocity close to the wall. Absolutely no sign of luminosity is seen in the region traversed by the exciting beam, except a trace on the inner wall of the tube where the velocity of the vapour is very low. At the centre of the tube the dark region extends 2 or 3 mm. above the beam. The form of the flame gives us a means of measuring the variation in the velocity of the vapour across a diameter of the tube. The "flame" appears at its best only when the Bunsen burner is at exactly the right height; if it is supplying heat too fast the fluorescence draws down into a flatter patch and may even enter the illuminated region. This results from too great back-pressure, which diminishes the velocity of the vapour.

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[*] Phillips, 'Roy. Soc. Proc.,' A, vol. 89, p. 39.

A photograph of the fluorescent "flame" is reproduced on Plate 5, fig. 4. This was taken with a glass lens, which excludes the powerful ultra-violet radiation (2536), which is also radiated by the "flame." The patch of light at the left is caused by the reflection and scattering of the exciting beam by the wall of the quartz tube, the fainter patch to the right marking the exit of the beam. Special precautions are necessary in the study of the phenomenon, with respect to this ultra-violet, monochromatic radiation. The "flame" must be photographed with a quartz lens and an objective prism of quartz, and the luminous patches of spark light scattered by the tube carefully screened off. Unless an achromatic quartz fluorite objective is used, the photographic plate must be inclined if the images corresponding to different wave-lengths are all to be in focus. This broadens the images of course. A photograph obtained in this way is reproduced in Plate 5, fig. 5. The "flame" evidently has the same general form in the monochromatic 2536 radiation, as in visible light. The relatively great intensity of this radiation is clearly brought out in the photograph.

If the spark is placed close to the bulb and the screen removed, the entire bulb appears filled with green fluorescent light, but if the eye is brought to the level of the mercury surface, a dark zone is seen between the free surface of the mercury and the luminous vapour, which reminds one strongly of the Crookes dark space in vacuum tubes. The width of this dark zone is about 1 mm. This is what we should expect, for the velocity with which the vapour leaves the mercury surface is only about one-third of the maximum velocity in the tube, on account of the larger cross-section of the vapour column in the bulb. If we had any means of measuring the velocity of the mercury vapour, we could at once determine the time intervals involved, but this is not easy. A rough approximation was made by calculating the volume of metallic mercury which distilled over in a given time (about 0·75 c.c. in six minutes) and determining the density by photographing the 2536 absorption line, comparing the width of the line with the widths shown in photographs made with a sealed tube at various constant temperatures. This was necessary as we cannot assume that the density of the vapour corresponds to the temperature at which the hot end of the distillation tube is held, for it depends upon the rate at which heat is actually supplied to the fluid mercury in the bulb. Estimates made in this way indicated that the average velocity was of the order of 10 metres per second. The velocity along the axis of the tube might easily be double this.

Owing to the uncertainty of these calculations, it seemed desirable to measure the time intervals directly, and a special type of high-speed phosphoroscope was designed for the further study of the phenomenon.

Some experiments were also made with an exhausted spherical bulb of quartz, 4 cm. in diameter, containing a few drops of mercury, and rotated at very high velocity. The whirling bulb was heated by a small blast lamp, and the spark focussed on the wall by a quartz lens. The fluorescent spot was not, however, displaced by the rotation, so far as could be seen. The reason for this will appear later, as it has been found that with great vapour density in bulbs the time interval between absorption and emission is much briefer than in the case of the inverted U-tube with distillation going on.

The resonance radiation excited by the monochromatic radiation of wave-length 2536 was next investigated. This is shown by the vapour of mercury at room-temperature, and probably does not depend upon distillation. This point has not, however, been proven as yet, for evaporation and condensation are considered as going on all the time at the surface of a liquid in contact with its saturated vapour. Resonance radiation should be looked for in a bulb containing no liquid mercury.

The first experiments were made with the inverted U-tube, the bulb being heated by a small vessel of hot water. No trace of any displacement of the radiating mass of vapour could be detected. A vertical tube, 2 cm. in diameter, and 10 cm. long, with flat ends (very highly exhausted) was then used, the upper end being provided with a cup of paper packed with cotton soaked with liquid air. The mercury at the bottom was at room-temperature. The cone of exciting radiation was obtained with a quartz monochromator and water-cooled mercury arc. The cone of resonance radiation was found in coincidence with the exciting cone, showing that the time interval between absorption and emission in this case was too small to be detected by this method.

We will now take up the experiments with the phosphoroscope, which yielded much more definite results.

The Synchrono-Phosphoroscope.

In order to determine with greater precision the interval of time elapsing between the absorption of the light and the emission, a spark phosphoroscope of special design was constructed. With this instrument I have been able to detect phosphorescence of a duration of less than 1/400,000 second, which is about ten times as brief as any observed phosphorescence of which I can find record.

A thin disc of Bakelite (similar to hard rubber), 45 cm. in diameter, was mounted on the shaft of a synchronous motor, operated by the same 60 cycle alternating current which fed the primary of a small 30,000 volt transformer. A small strip of thin sheet brass, 3 cm. long, bent out into two points, was screwed to the disc (parallel to a radius) near the rim. Two pointed brass wires, wound in short spirals and mounted on a block of hard rubber, were brought up close to the points on the disc, and the circuit arranged as shown in Plate 5, fig. 2. K is a capacity of two small Leyden jars, A the illuminating spark. A few trials are necessary to find the proper place at which to mount the pointed rods, in order to complete the circuit at the moment when the potential of the transformer is near a maximum. By carefully adjusting the distance between the fixed and rotating points, it is possible to fix the timing of the sparks so accurately that no motion of the little brass strip (illuminated by the light of the sparks which pass between its points and the wires) can be detected. The speed of the disc was 1800 revolutions per minute, yet it appeared absolutely stationary in a dark room. If the adjustment of the gaps is not right, the brass strip appears to dance up and down, in an irregular manner, with an amplitude of perhaps a millimetre, and the satisfactory operation of the instrument, at least for the study of the briefest time intervals, depends upon the complete elimination of this irregularity. The elasticity of the spirals obviates the danger of breaking the points by actual contact, which occurs in making the adjustment. A radial slit, 1 mm. in width, was cut in the disc near the rim, and a small quartz bulb containing a droplet of mercury, or the U-tube previously described, was mounted behind the disc and viewed through the slit, as the disc revolved. The illuminating spark (between aluminium rods) was mounted close to the quartz bulb.

It was found that, if the eye was brought up close to the disc at such a point that the sparks flashed at the moment when the moving slit crossed the pupil of the eye, the outline of the bulb or tube, illuminated by the spark light, could be seen, but no trace of the green phosphorescence of the vapour could be detected. This came into view when the eye was moved a trifle in the direction in which the slit was moving, the bulb disappearing, of course. It was found that the distance between these two positions was so small that the diameter of the pupil of the eye gave trouble, and a second slit was mounted close to the disc, and arranged so that it could be moved to the right or left by small increments. When everything was in the best adjustment, it was found that a movement of the second slit through a distance of about 2 mm. brought the phosphorescence into view, in the case of the inverted U-tube, while, with the bulb, the distance was so small that some uncertainty was felt as to whether the effect was really present. The reason for this will appear presently. This means that the time interval between the flash of the spark and the emission of the fluorescent light is of the order of 1/20,000 second.

The operation of the phosphoroscope in this form was not quite satisfactory, owing to the fact that very narrow slits had to be used for the measurement of the shortest time intervals, a disadvantageous circumstance in consideration of the comparative faintness of the light sources employed. A great improvement in the performance of the instrument was obtained by cementing a small lens (1 cm. in diameter and 3· cm. focus) in a hole in the disc near the rim. This lens formed a real image of the source of light, which was viewed with a short focus lens or eyepiece, the image, of course, moving with the velocity of the lens. The lens is inserted in such a position on the disc as to ensure its moving in a nearly horizontal direction at the moment the spark occurs, *i.e.*, the lens should be at the top of the disc when in the sparking position. It was thought that this device would show the motion of the fluorescent vapour by giving an oblique image of a vertical slit, backed by the fluorescent "flame." Owing to the inconvenience of operating the mercury tube close to the disc, it was placed at a distance of about a metre, and an image of it projected at a point about 10 cm. in front of the small lens, with the disc set in the sparking position. This arrangement gave most satisfactory results. The vertical image of the slit was plainly visible by the spark light scattered by the walls of the quartz tube, while the green oblique image appeared completely detached from it, and inclined at an angle depending upon the velocity of the vapour, as shown on Plate 5, fig. 6. We have here complete data for determining the period of darkness which precedes fluorescence, by two different methods:—

First: We measure the distance between the base of the vertical image of the slit and lower end of the oblique band. This was found to be 2·5 mm., and, since the image moves 1 mm. in 1/39,000 second, the time interval between the excitation and the emission of the first fluorescent light is 1/15,600 second.

Second: By measuring the obliquity of the displaced image we can calculate the velocity of the vapour. The flash of light from the spark passing through a small hole gives an instantaneous excitation to a small mass of mercury vapour which is moving upward with a high velocity. By the time it bursts into luminosity it has already moved up a short distance, and as it continues to ascend, the moving lens carries its image to the right. The tangent of the angle which the oblique image thus formed makes with a horizontal line is the ratio of the velocity of the vapour to that of the lens, and this angle was found to be about 23°. This gave 17 metres per second as the velocity of the vapour. Observations of the fluorescent flame showed that the luminosity commenced about 1·5 mm. above the excited region. This gives us for the time interval 1/11,400 second, a value somewhat smaller than the one obtained by the first method. The former is probably more nearly exact. A small bulb was now substituted for the inverted U-tube, heated by a column of hot air rising from an asbestos chimney. The spark was placed close to the bulb, and the fluorescence occurs chiefly on the inner surface on the side facing the spark (superficial fluorescence) owing to the density of the vapour.

The whole slit was simultaneously illuminated by the fluorescent light under these conditions, and it was expected that the image seen with the moving lens would appear as in Plate 5, fig. 6. It was found, however, that the band of green fluorescent light was joined to the image of the slit formed by the light (white) of the spark scattered by the walls of the bulb. This explained at once the difficulty found in getting results by the first method, in which the bulb was viewed through a narrow slit in the disc. The greater density of the vapour in this case evidently reduces the time interval between absorption and emission to something less than 1/40,000 of a second, as this would give a displacement of a millimetre, which could be observed without difficulty. A vertical tube of quartz about 2 cm. in diameter and 10 cm. long, was now substituted for the bulb, and the pool of mercury at the bottom heated by a small flame. The spark was placed close to the front wall of the tube. The phosphoroscope now showed a beautifully displaced band, as shown on Plate 5, fig. 7. The time interval in this case was about the same as in the other experiment, 1/15,000 second.

Experiments with Phosphorescent Solids.

The phosphorescence of solids can obviously be investigated by the same method, but a simpler arrangement was found preferable, namely, to make the solid itself the moving source. Uranium glass was examined first. A thread of the glass measuring about 0·1 mm. in diameter was drawn out and a small fragment cemented to the edge of the disc, about 5 mm. projecting beyond the rim. The spark was placed as close as possible to the glass thread, behind a screen of black paper, which kept the direct light out of the eye. On setting the disc in rotation, and examining the thread of uranium glass with a short focus lens, it was found that the broad green phosphorescent band joined the white image of the thread (formed by refracted and reflected light). I feel sure that a dark band between the two 0·1 mm. wide could have been detected if it existed. This proves that the time interval in this case must be less than 1/400,000 second.

Barium platino-cyanide was next investigated; a long crystal, 0·5 mm. wide, showed no trace of phosphorescence, the crystal appearing quite sharp in its brilliant green fluorescent light; a needle-shaped crystal, 5 mm. long and 0·1 mm. in diameter, was then cemented to a small strip of thin lantern slide glass, with collodion, and the glass plate attached to the rim of the disc with sealing wax, as shown in Plate 5, fig. 3. This gave the very surprising result that the total duration of the phosphorescence was only about 1/400,000 second. The crystal appeared accompanied by a phosphorescent band of a width almost exactly equal to that of the crystal (0·1 mm.). This came pretty close to being fluorescence.

A number of other substances were examined, and the results are given in the following Table :—

Substance.	Width of phosphorescent band.
Uranium glass	One-quarter of revolution of disc.
Willemite	Three-quarters of revolution of disc.
Balmain paint	Blue-green phosphorescence lasting 1/40,000 second. Violet phosphorescence of long duration too faint to appear.
Anthracene	Small crystals cemented to glass, ¼ mm. (1/160,000 second).
Barium platino-cyanide	0·1 mm. (1/400,000 second).

Fluorescent Solutions.

In the case of liquids which are available in sufficient bulk, another method is preferable, for we can give a liquid jet a much higher velocity than anything that can be obtained with a phosphoroscope. I made a few experiments with solutions of fluorescene, using jets of comparatively low velocity (having no facilities for high pressure), and focussing sunlight on them. No displacement of the fluorescent spot could be detected.

Some experiments were then made at the University of Wisconsin, in collaboration with Prof. C. E. Mendenhall, during my visit to Madison in December. We used a high pressure, six-cylinder pump, and obtained a jet velocity of about 200 metres per second, with a fine glass nozzle about

0·2 mm. in diameter. More recently, Prof. Mendenhall has increased the velocity to 230 metres per second, and, by blackening one side of the jet tube, leaving a small clear space for the entrance of the sunlight, has assured himself that there is no displacement as great as 0·1 mm. (observing the fluorescent patch with a short-focus lens). This means that the duration of the fluorescence is less than 1/2,300,000 second.

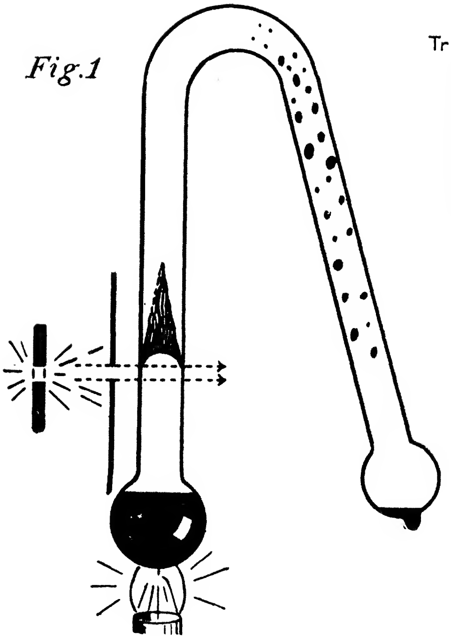
In the case of the fluorescence of solutions, however, we must bear in mind that the emission of light is accompanied by, if not the direct result of, the destruction of the fluorescent body. This has been known for some time in the case of certain substances (anthracene, for example), and its general application has recently been pointed out by Perrin, who showed that thin films of fluorescent solutions were bleached by the action of light, and lost their power of exhibiting fluorescence.

I have examined this question on a somewhat larger scale, concentrating sunlight with a large lens, and have found that fluorescene, eosine, rhodamine and other similar bodies are transformed into non-fluorescent coloured solutions, with absorption bands of different form from the original bands, and located in different regions of the spectrum. If substances of similar optical properties can be prepared by chemical or electrical means (oxidation or reduction, for example) from the original substances, we shall be able to tell, with tolerable certainty, just what change results from the action of the light. It seems a remarkable hypothesis, at all events, that the emission of light in these cases results from a molecular explosion produced by the radiation, rather than from the return of an expelled electron. If this is the case, the brevity of the phenomenon is accounted for.

There seems to be one rather curious circumstance, to which attention has never been drawn so far as I am aware, namely, that all fluorescent solutions are solutions of organic compounds. The only exception to this rule that I know of is in the case of very concentrated solutions of some of the uranyl salts, which show a very feeble greenish fluorescence when illuminated in a dark room with a powerful beam of concentrated sunlight passed first through dense cobalt glass.

The feebleness of the fluorescent light, and the great concentration of the solution, suggests that only a very small percentage of the molecules are engaged in the process, and the idea occurs to one as to whether the phenomenon may not perhaps be associated with the natural breakdown of uranium. These matters will be more fully discussed in another paper.

Fig. 1



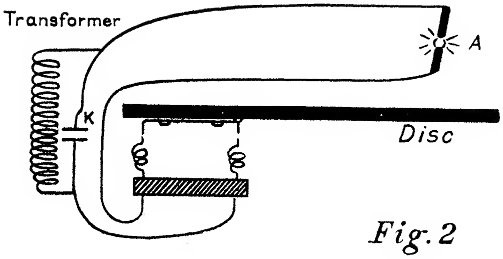


Fig. 2

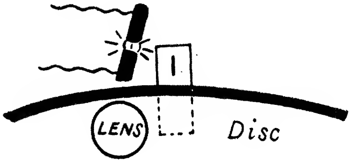


Fig. 3

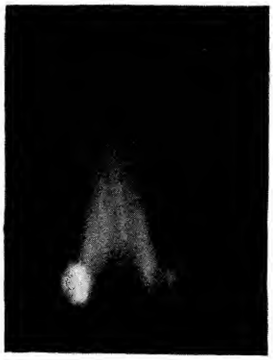


Fig. 4

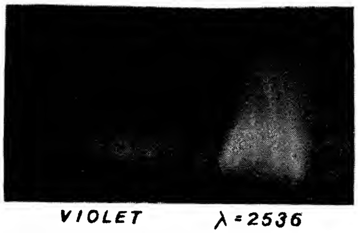


Fig. 5

Fig. 6

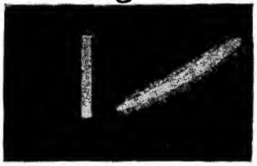


Fig. 7

Application of the Method of Abraham and Lemoine to the Study of Phosphorescence.

This method (see my 'Physical Optics,' p. 549) enables us to deal with time intervals of the order of 1/400,000,000 second. It depends upon the double refraction of bisulphide of carbon or nitro-benzol in an electrostatic field. Two plates are immersed in the liquid, and these form the plates of a condenser, which discharges at a spark gap placed behind a nicol prism and viewed through a second nicol, placed at extinction, through the space between the plates of the fluid condenser.

If the spark is close to the condenser, the light reaches it before the double refraction has disappeared, and is therefore passed by the second nicol. If, however, the light is made to traverse a path of about 2 metres, by reflecting it from a mirror, the double refraction has disappeared during the time taken by the light to traverse this distance, and the image is no longer visible.

With bisulphide of carbon the restored light is so feeble that it was obvious that the light of a crystal of barium platino-cyanide, placed close to the spark, would not be seen.

With nitrobenzol, in which the Kerr effect is sixty times as powerful, however, there seemed to be some hope of getting results. It was found that even freshly distilled pure nitrobenzol conducted too well to form a condenser. Phosphorus pentoxide changed it to a deep red liquid in a few hours, and lime did not prove effective in removing the traces of water which were assumed to give the trouble. Dehydrated copper sulphate, poured while still red-hot into the liquid, and shaken up with it at intervals for a few days, brought it into excellent condition. With this I had no difficulty in seeing the greenish image of a crystal of barium platino-cyanide placed very close to the spark. If it had remained dark for a period of say 1/10,000,000 of a second, its light would not have been passed by the second nicol.

There is room for further work along these lines. So far as I am able to say now, it appears that the duration of the double refraction with nitrobenzol is considerably greater than in the case of carbon bisulphide, for I could not get the spark to disappear even with a path of 15 metres.

I have been aided in this investigation by a grant from the Rumford Fund of the American Academy of Arts and Sciences.

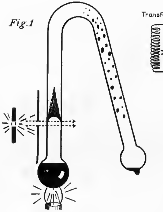


Fig.1

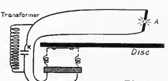


Fig. 2

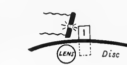


Fig. 3

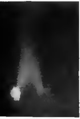


Fig. 4

Fig. 5

Fig. 6

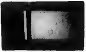


Fig. 7